

The samples were removed for the press and allowed to cool to room temperature. Peel strength or adhesion was measured on the samples in accordance with ASTM D 1876 (T-Peel test). An Instron™ Model 1125 tester, available from Instron Corp., set at a 100 min/min crosshead speed was used as the test device. The peel strength was calculated as the average load measured during the peel test. The measured peel strength from Example 1 is reported in Table 1.

#### Comparative Example C1

In Comparative Example C1 a composite sample was prepared and tested as in Example 1, except that no extruder mixed adhesive film was used between the polyamide-12 and THV 500 film. The test results for Comparative Example C1 are reported in Table 1.

#### Example 2

In Example 2, a sample was prepared and tested as in Example 1, except that the THV 500 was replaced by E-14660 from Dyneon LLC. This material is a terpolymer of tetrafluoroethylene, hexafluoropropylene and ethylene. Test results for Example 2 are reported in Table 1.

#### Comparative Example C2

In Comparative Example C2, a sample was prepared and tested as in Example 2, except that no extruder mixed adhesive film was used between the polyamide-12 and E-14660 layers. Test results for Comparative Example 2 are reported in Table 1.

Example #	Composite Construction	Peel (Kg./2.54 cm)	Failure Interface
1	1: Polyamide-12 2: Tie Layer 3: THV 500	11.4	THV Cohesive Failure
C1	1: Polyamide-12 2: THV 500	0.4	Interfacial Failure
2	1: Polyamide-12 2: Tie Layer 3: E-14660	14.5	HTE 1500 Cohesive Failure
C2	1: Polyamide-12 2: E-14660	7.7	Interfacial Failure

The complete disclosures of all patents, patent applications, and publications are incorporated herein by reference as if individually incorporated. Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

#### Example 3

In Example 3, a mixture containing 49.5% Grilamid™ L25W40X black polyamide 12 (EMS American Grilon, Sumter S.C.), 49.5% Grilamid™ L20HV1, said to be a polyamide 12 having an excess of primary amine end groups (EMS American Grilon, Sumter, S.C.), and 1% P152 was added by an Accurate™ dry material feeder (Accurate Inc., Whitewater, Wis.) to a 25 mm corotating Behrstorff twin screw extruder (Behrstorff Charlotte, N.C.) operating at a screw speed of 250 rpm and die temperature of 220 C. The resulting extruded product was a modified polyamide 12 that had at least one pendant phenolic group and pendant primary

and secondary amine groups. The extruded strand of modified polyamide 12 was cooled in a water bath and pelletized at a rate of approximately 10 Kg/hr.

The modified polyamide 12 was then coextruded with THV 500 into two layer tubing. The modified polyamide 12 was the cover and the THV 500 was the inner layer. The THV 500 was extruded on a 1 inch diameter Harrell extruder with a temperature profile of 220C, 230, 235, 245, and 250 C barrel temperatures. The inlet flanges were set at 205 and 190 C. The modified polyamide 12 coverstock was extruded on a 2 inch Harrell and a temperature profile 200 C, 200, 200, 200, and 200 C barrel temperatures. The inlet flanges were set at 205 and 195 C. A 2 layer Guill head was used to extrude the tubing. The tooling consisted of a 1 inch ID die and a 0.745 inch OD pin and a 1.760 inch land. The head temperature bands were set at 195 C and the die zone was at 220 C. The overall rate was 67 g/min, and the tubing was vacuumed sized to a final dimension of approximately 6 mmx8 mm.

The adhesion between the two layers was observed to be excellent in that the modified polyamide layer and THV 500 layer of the coextruded tube could not be physically separated.

What is claimed is:

1. A composite comprising:

- a first layer of a substantially non-fluorinated thermoplastic polymer having at least one pendant phenolic group, and a base, and
- a second layer of a fluoropolymer adhered to the first layer, provided that when the pendant phenolic group of the substantially non-fluorinated thermoplastic polymer is derived from the reaction of a functionalized olefin with a bisphenol, substantially no organo-onium is present.

2. The composite of claim 1 wherein the fluoropolymer comprises interpolymerized units selected from the group consisting of vinylidene fluoride and fluorinated monomers which, when polymerized, form a polymer microstructure sequence similar to polymerized vinylidene fluoride in that the polymer has a carbon-bonded hydrogen atom between carbon-bonded fluorine atoms.

3. The composite of claim 2 wherein the vinylidene-fluoride containing fluoropolymer is comprised of interpolymerized units derived from (i) at least one fluorine-containing monomer selected from the group of vinylidene fluoride, trifluoroethylene, 1-hydropentafluoropropylene, 2-hydropentafluoropropylene, and, optionally, (ii) at least one monomer copolymerizable therewith.

4. The composite of claim 3 wherein the monomer (ii) is selected from the group consisting of a fluorine-containing monomer; a fluorine-free, unsaturated olefin monomer; an iodine- or a bromine-containing unsaturated olefin monomer; and a combination thereof.

5. The composite article of claim 4 wherein

- the fluorine-containing monomer is selected from the group consisting of hexafluoropropylene, tetrafluoroethylene, chlorotrifluoroethylene, a fluorinated vinyl ether, and a fluorine-containing di-olefin;
- the fluorine-free, unsaturated olefin monomer is selected from the group consisting of ethylene, propylene, and butadiene; and
- the iodide- or bromide-containing unsaturated olefin monomer is selected from the group consisting of bromodifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene, and 4-bromo-3,3,4,4-tetrafluoro-1-butene.

13

6. The composite of claim 1 wherein the fluoropolymer is a terpolymer of ethylene, hexafluoropropylene and tetrafluoroethylene, and having an ethylene content of at least 11% and a hexafluoropropylene content of at least 22%.

7. The composite of claim 1 wherein the fluoropolymer is a terpolymer of ethylene, hexafluoropropylene and tetrafluoroethylene, and having a melting point of less than 168° C.

8. The composite of claim 1 wherein the fluoropolymer is a blend of (i) a fluoropolymer which contains vinylidene fluoride containing polymer and (ii) a non-vinylidene fluoride containing fluoropolymer.

9. The composite of claim 1 wherein the fluoropolymer is a fluoroplastic.

10. The composite of claim 1 wherein the fluoropolymer is a fluoroelastomer.

11. The composite of claim 1 wherein the fluoropolymer is pre-dehydrofluorinated.

12. The composite of claim 1 wherein the fluoropolymer is surface treated.

13. The composite of claim 1 wherein the substantially non-fluorinated thermoplastic (a) is selected from the group consisting of polyamides, polyimides, polyolefins, polystyrenes, polyurethanes, polyesters, polyacrylates, polymethacrylates, polyketones, polyureas and polycarbonates.

14. The composite of claim 13 wherein the substantially non-fluorinated thermoplastic is a polyamide.

15. The composite of claim 14 wherein the polyamide is nylon-12.

16. The composite of claim 14 wherein the polyamide is a zinc chloride resistant polyamide.

17. The composite of claim 16 wherein the base further comprises an organo-onium compound.

18. The composite of claim 16 wherein the base is 1,8-diazabicyclo [5,4,0]undec-7-ene.

19. The composite of claim 1 wherein the base is selected from the group consisting of amine compounds, hydroxide compounds and alkoxide compounds, and combinations thereof.

20. The composite article of claim 1 further comprising (c) a second substantially non-fluorinated polymer component adhered to the first layer.

21. The composite article of claim 20 wherein the component (c) is selected from a polyamide, a polyimide, a polyurethane, a polyolefin, a polystyrene, a polyester, a polycarbonate, a polyketone, a polyurea, a polyacrylate, and a polymethacrylate.

22. The composite article of claim 21 wherein component (c) is a polyamide.

23. The composite article of claim 22 wherein the polyamide is nylon-12.

24. The composite article of claim 22 wherein the polyamide is a zinc chloride resistant polyamide.

25. The composite article of claim 20 wherein the component (c) is an elastomer.

26. The composite article of claim 1 which is shaped.

27. The composite article of claim 26 selected from the group of a wire coating, a tube, a container, a sheet, a cable jacket and a film.

28. The composite article of claim 1 wherein the substantially non-fluorinated thermoplastic polymer further has at least one pendant primary or secondary amine group.

29. The composite article of claim 28 wherein the substantially non-fluorinated thermoplastic polymer is a polyamide.

30. The composite article of claim 29 wherein the polyamide is nylon-12.

31. The composite article of claim 29 wherein the polyamide is a zinc chloride resistant polyamide.

14

32. The composite of claim 1 further comprising additives in at least one of the components.

33. The composite of claim 1 wherein the pendant phenolic group is a substituted or an unsubstituted phenolic group.

34. The composite of claim 33 wherein the pendant phenolic group is an unsubstituted phenolic group.

35. The composite of claim 33 wherein the pendant phenolic group is a substituted phenolic group.

36. The composite of claim 33 wherein the substantially non-fluorinated thermoplastic polymer has pendant substituted and unsubstituted phenolic groups.

37. A multi-layer polymer article comprising, in order: a first layer of a fluoropolymer;

a second layer comprising a substantially non-fluorinated thermoplastic having

- (i) one or more pendant phenolic groups, and
- (ii) a base;

a third layer comprising a substantially non-fluorinated polymer, provided that when the substantially non-fluorinated thermoplastic polymer of the second layer comprises a polyolefin derived from the reaction of a functionalized polyolefin and a base, substantially no organo-onium is used.

38. A shaped composite article of claim 37.

39. The shaped article of claim 38 selected from a sheet, a hose, a tube, a sheet, a film, a wire coating, a cable jacket, and a container.

40. The multilayer article of claim 37 wherein the substantially non-fluorinated thermoplastic polymer of the second layer further has at least one pendant primary or secondary amine groups.

41. The multilayer article of claim 40 wherein the substantially non-fluorinated thermoplastic polymer of the second layer is a polyamide.

42. The multi-layer article of claim 41 wherein the polyamide is nylon-12.

43. The multi-layer article of claim 41 wherein the polyamide is a zinc chloride resistant polyamide.

44. A method of adhering a substantially non-fluorinated polymer to a fluoropolymer comprising

- (a) providing (i) a substantially non-fluorinated thermoplastic polymer having at least one pendant phenolic group thereon, (ii) an organic or inorganic base, and (iii) a fluoropolymer,

(b) at least partially reacting the phenolic group with the base to form a modified substantially non-fluorinated thermoplastic polymer,

(c) forming a composite article comprising the fluoropolymer in contact with the modified thermoplastic polymer, and

(d) subjecting the composite article to pressure, and/or temperature conditions adequate to bond the fluoropolymer to the modified thermoplastic polymer,

provided that when the substantially non-fluorinated thermoplastic polymer comprises a polyolefin derived from the reaction of a functionalized polyolefin and a base, substantially no organo-onium is used.

45. The method of claim 44 wherein the substantially non-fluorinated thermoplastic polymer has at least one pendant primary or secondary amine group.

46. The method of claim 45 wherein the substantially non-fluorinated thermoplastic polymer is a polyamide.

47. The method of claim 46 wherein the polyamide is nylon-12.

48. The method of claim 47 wherein the polyamide is a zinc chloride resistant polyamide.

\* \* \* \* \*